The 1st International Joint Conference on Science and Technology (IJCST) October 12-13th, 2016, Bali, Indonesia

EXTRACTION of PECTIN FROM COCOA PEEL WASTE

Rudy Laksmono. W[1] Soemargono[2],and Edi Purnomo Sasongko[3]
[1] Department of Energy Security, Faculty of Defense management, Indonesia Defense Univercity
[2] Department of Chemical Engineering, Faculty of Technology Industry UPN "Veteran" East Java
[3] Department of Agrotechnology, Faculty of Agriculture UPN "Veteran" East Java
E-mail: rlwidayatno@yahoo.com

ABSTACT

The chocolate tree or plant is a kind of cocoa plantations that are a mainstay for Indonesia's commodities. As much as 95% cocoa plantation owned by individual farmers who constitute about 1.7 million farmers throughout Indonesia with total production of cocoa beans nationwide in 2012 reach 450,000 tons. According to the National Statistics Agency (BPS) monthly production in 2012 for plantations in Indonesia reached 77,360 tons per month. The peel cocoa itself now as a mixed material animal feed and as a waste not utilized. In the peel cocoa contained pectin about 7-12%. The pectin material is required in the food product industry and also for pharmacy product which have an economic value than the cocoa peel as a waste. The research method used is an experimental in the laboratory with the extraction of cocoa peel continuous process. Main reactor unit consist of a transparent column from flexy glass material completely with the "oblique incline bubble" as a function for a barrier flow and bubble breaker. The production process has been implemented which include variations in the speed of the flow of cocoa peel paste that determine the residence time of material in a reactor, operating temperature, and the levels of citric acid as a chelating agent. The residence time is calculated by the equation: $t = \frac{12931{,}22G^{-0{,}3306}}{L}$ (minutes), with G = gas flow velocity and fluid flow velocity L = ingredients (cocoa peel porridge + citric acid). Comparison of cocoa porridge (100 grams in 1000 mL of water) and citric acid ratio is 1:1 with the variation of temperature and concentrations of citric acid. The best results are obtained with the highest metoksil levels based on, namely 5.332% achieved at residence time 82 minutes, the temperature of 70 ^{0}C, concentrations of citric acid 0.1 N with 5,4186% yield.

Keywords: pectin, cocoa peel waste, incline baffle reactor

Introduction

Indonesia as an agricultural country has a greater variety of crops. One type of plantation crops are cocoa. This plant is a commodity for the State of Indonesia. From the research that has been done on the data showed that the cocoa peel achieved 60% by weight of cacao fruit. Cocoa peel reached 3 times from the weight of the seeds. The existence of cocoa peel in this area only a part is used as an animal feed. Cocoa peel dry showed pectin contain between 6-12%, whereas in the pulp of cacao are pectin contain at 1%. Pectin necessary for the food industry, pharmaceutical, medical, and body care (CP Kelco, 2013).

Pectin is a polymer from D-galacturonic acid linked by β-1,4 glycosidic bond. D-galacturonic acid has the same structure as the structure of D-galactose, the difference lies in the C6 primary alcohol groups which have carboxylic groups (Hart et al, 2003) as shown in Figure 1.

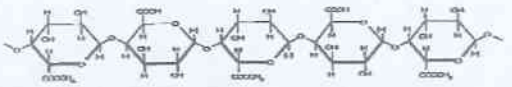


Figure 1. Acid Pectinat Compound or Pectin

Acid in the extraction of pectin is used for the hydrolysis process protopectin be water-soluble pectin or pectin freed from ties with other compounds, such as cellulose. Meyer (1978) states that protopectin being pectin is a macromolecule which has a high molecular weight, formed between the molecular chains of pectin with one another or with other polymers. Protopectin insoluble as in the form of calcium-magnesium salts pectinat. Protopectin leaching process becomes pectin occurs due to replacement of calcium and magnesium ions by hydrogen ions or because the severing of ties between pectin and cellulose. The higher concentration of hydrogen ions (pH), the lower the ability to replace calcium and magnesium ions, or cut ties with cellulosic also high and

soluble pectin will increase. In addition to pH, temperature process is very influential on the results obtained. Pectin extraction takes place by the hydrolysis, meaning that the release of water (H_2O) in the extraction process. It can be said that the extraction takes place, accompanied by a chemical reaction. Such a process, in addition to the concentration, temperature and eddy stirring very influential. Temperature affects the speed of chemical reactions, as well as eddy / agitation (Levenspiel, 1972). Eddy reactor sectional oblique column happens to blowing inert gas as a nitrogen gas. Gas that will be split by the serration of sloping bulkhead mounted. Thus, the concentration, temperature and eddy heavily influence the extraction of pectin from cocoa peel.

Extraction of pectin research has been done, such as from chayote (Daryono, ED, 2012), mango peel (Malviya R., et al., 2010), Pulp Pineapple (Puspita, D., et al., 2008), Dragon Fruit (Ismail, NSM, et al., 2012). Likewise pectin from cocoa peel has been done by Irnawati et al. (2006), Susilowati et al (2010). Irnawati et al. (2006) studied the cocoa peel based on their age of fruit. From the researchers use an average of hydrocloride acid (HCl) as an extractor. The other side, Sari, E., et al., (2012) to improve the quality of pectin from cocoa peel by adding $NaHSO_3$ with HCl as an extractor. However there are using citric acid (Malviya R., et al., 2010) and ammonium oxalate / oxalic acid (Ismail, N. S. M., et al., 2012). Pectin from aloe vera are researched by Gentilini, R., et al (2014) conducted enzymatically by using microwave as activation and sodium citrate as a chelating agent. All the research is done in a "batch" system completed with stirring. The process continuously for extraction of pectin has not been done. Various types of continuous reactors are widely used, starting as simple as flow stirred tank reactor. The other type, the column reactor including reactors bubble, fluidized bed or moving bed reactor, until the trickle-bed reactors both for the reaction homogeneous or heterogeneous (Harriot, P, 2003; Zehner, P and Kraum, M, 2000; Rase, HF, 1977). Shin, S. B. et al (2007) conducted a computer simulation optimization with the multi tube reactor is a continuously for reaction-reaction of hydrocarbons.

Extractor can also be classified into the reactor. The simplest extraction using a soxhlet run semi-continuously. Extraction continuously too many types and consumer. As performed by the Holder, R. W (1973) who studied the liquid-liquid extraction. Likewise M.C. Goldberg, et al (1971) who studied the organic material from water extraction (extraction of organic materials from water) continuously. Bhornsmithikun, V, et al (2010) who studied Continuous extraction of prebiotics from jackfruit seeds. Kim, K. H, et al (2001) studied the hemisellulose continuous extraction with the flow in opposite directions even though the process is done is hydrolysis followed by fermentation to form ethanol. Stangle and Mahalingam using different reactor types, namely foam reactor for heterogeneous three-phase reaction. It was intended to expand the surface area contact between liquids and solids. Type the reactor and extractor studied their performance to find good condition and the best results.

Type bubble column reactor are very popular because its operation is simple, easy, space requiring a relatively narrow, and the cost is relatively cheap. A process that can be implemented in a batch or continuous system with directional streaming (cocurent) or bidirectional (countercurrent). In a continuous process, the flow pattern in the bubbles pipe reactor often impaired primarily on the flow of gas at high speed. It causes the slug flow patterns and "churn turbulent" (heterogeneous regimes) undesirable (Shah et al., 1982). An insulated bubble pipe reactor oblique expected to reduce the problem, because the gas flow patterns with incline baffle serves as a bubble breaker that can replace mechanical stirrer (Soemargono, 2007). In this reserach, the rector column tilted bulkhead used as an extractor, the extraction of pectin in the fruit cocoa peel. In this study is expected to provide an overview of performance insulated sloping fields marked with the results obtained can be used to design the reactor / extractor minimum scale plant if needed.

Methode

Pectin research extract with continuous system is doing in the pilot scale reactor. The main reactor namely is "oblique incline bubble". The raw materials obtained from the Farmers Group "Guyub Santoso" as a partner in Blitar. Cocoa peel is chopped before pulverized using a grinder or "blender" with the addition of water as much as 10 times the weight of raw material (a ratio of 1:10). As a reagent is citric acid. Alcohol 96% is used as a deposition of pectin. The chemicals were obtained from a distributor of chemicals in Surabaya.

the equipment used research is a sketch at Figure 2. The main tool in the form of reactor incorporating sloping bulkhead completed with heating jacket, a feed regulator valve, air intake and discharge pot, thermometer, and rotameter. Medium heating jacket with water diverted from the tank water heater with circulation. Devices research reactor made of from glass that is resistant to temperatures over 80 ° C, 5 cm in diameter, heating jacket diameter of 10 cm and 150 cm tall columns that bulkhead mounted oblique and asymetric place and jagged. It is intended to enable the mixing well. On top there is a reactor where the entry of the feed, a thermometer, and a gas expenses, while the bottom of the reactor connected with a part of the

delivery and the introduction of gas / air. Columns surrounded by larger-diameter pipe that serves as a cover heater with a water medium diameter of 10 cm. Gas / air is used as the medium turbulent to perfect mixing occur during the column reactor.

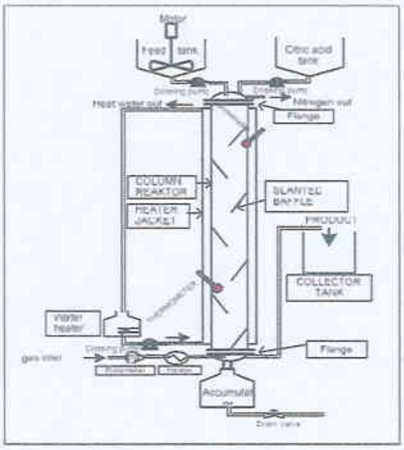


Figure 2. Research equipment circuit

The process of extracting pectin.

The process is continuous in a sectional oblique column with the observation of the results is influenced by: the material flow velocity, the ratio of raw materials and solvent, the pH of the solvent, the process temperature and process time.

Procedure:

1. Preparation of raw materials : Powdered cocoa peel weighed 200 grams and add water until volume two (2) liters. Citric acid used is citric acid with special concentration (normality) made two (2) liters.
2. Extraction : One liter slurry mixed cocoa peel and 1 liter certain normality citric acid and then loaded into the reactor until a half more than the height of the column. Followed by the air flow at a certain speed. Along with that fluid flows from the feed tank with a ratio of 1: 1 between the suspension cocoa peel with certain normality citric acid, and the heater turned on. Feed rate of each flow is set with the help of "dossing pump". Temperature is controlled with a water heater that is regulated by a controller. The process is made until the process conditions is achieved, ie the desired temperature has been reached, the results came out the pH remains. After that the process was continued for 20-30 minutes to accommodate the results, then discontinued. After the extraction process is complete, the results continued with the process fluid coagulation, sedimentation, and drying of pectin.
3. Thickening : Fluid is heated at a temperature of 90 - 95^{0}C, stirring until its volume by half. Results obtained is called the filtrate concentrated and do the sedimentation process.
4. Precipitation of pectin is done by adding acid alcohol, i.e every 100 ml of 96% alcohol acidified by adding 1 ml of concentrated citric acid. The addition of acid alcohol into the liquid filtrate as much as 1.5 times that of the existing materials. Then the solution is allowed to stand for 10-14 hours (overnight) to obtain precipitate pectin. After the deposition of pectin is separated from the liquid through a suction sieve. The results obtained so-called acid pectin
5. Washing of Pectin : Into pectin sour coupled with 96% alcohol in moderation while stirring. Then filtering with suction seive. This is done several times until pectin is white.
6. Drying. The washed pectin was dried at 600C for 6-10 hours. The results obtained so-called dry pectin weighed to obtain the yield and analyzed metoksil concentrate.

Results pectin solids weighed and analyzed for yield is calculated and analysed metoksil concentrate. The yield:

The equqtion of yield calculation :

$$\text{Yield} = \frac{\text{wight of Solid result}}{\text{initial weight}} \, x \, 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1).$$

Initial weight solids is calculated by:
The initial solid = yield collection time x velocity of cocoa pulp x 10% ..... (2).
Methoxyl concentration :
Amount 50 mg solids pectin combined with 25 mL of 0.25 N NaOH solution, shake and let stand for 30 minutes. After that add indicators phenolpthalin and 25 mL of 0.25 N HCl solution then titrated with NaOH 0.1 N until it changes color (pink) and record volume mL NaOH required. Methoxyl levels calculated by the equation :

$$\% \text{ metoksil} = \frac{\text{mL alkali x N alkali x 31}}{\text{sample weight}} \times 100\% \quad \ldots\ldots (3).$$

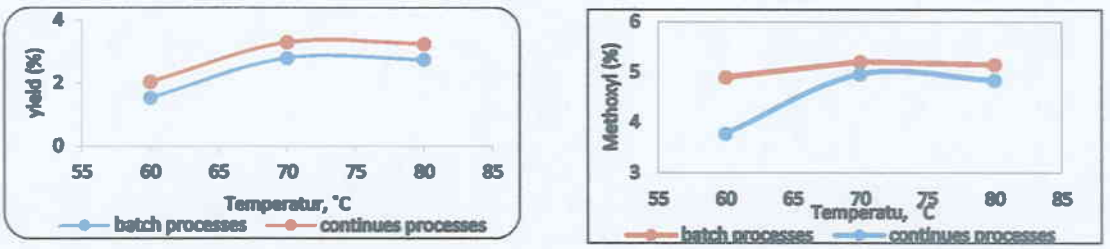
Result and Discussion

To determine the performance of equipment taken some trial data continuously and is accompanied by the process in "batch" under the same conditions. Continuous process taking place at a fix flowrate of gas remains in each trial amounted to 2880 mL/min with a suspension volume column contains as much as 2560 mL. Thus, the residence time of the suspension in the column only depends on the speed of the feed flow, mL/min. The results obtained are listed in the table I and II were clarified by Figures 3 and 4.

Table I. The effect of temperature on the yield and content of methoxyl at the time of 70 minutes and 0.1 N citric acid

Temperature	Rendemen (%)		% Metoksil	
°C	Continue	Batch	Continue	Batch
60	3,0638	1.7045	4.90	4.40
70	5,2973	3.7311	5.21	4.96
80	5,2465	3,6549	5.15	4.84

From the acquisition of data can be compared with the results continuously conducted in a "batch". Table 1 is made clear by Figure 3 (a) and (b).



(a) (b)

Figure 3. Efect of temperature with (a) Yield and (b) Methoksil

In the continuous process, the yield of pectin which produced slightly higher than with the process of "batch" process with the same condition. Likewise, the effect of temperature on the results of methoxyl (Figure 5), although at 60 ° C difference is quite far away. From observation, the turbulence generated by the nitrogen gas flow in a column equipped with a incline baffle bulkhead is perfect compared to the way "batch" with stirring. In the process of "batch" in a stirred tank equipped with barriers (baffle) shows that the perfect eddy that occurs only at the bottom near the pedal stirrer. This is because the suspension cocoa peel has a high viscosity.
In the process continuously, the results obtained liquid looks clear at the top. It is more advantageous than the process of "batch". The first advantage, advanced process for obtaining a solid pectin without filtering. The second Advantage, there is no fluid loss from ending up in a cloth filter. The results of field trials, the loss of fluid that is in the process of screening results, ending up in a cloth filter and process the rest of the cocoa solids peel is quite high, which is between 20% - 27.5%.
Study of Residence Time:

As a reference in the study on the variation of the residence time, do calibration used in subsequent implementation as described in the following list.
The equation of residence time :

$$t = \frac{1293122G^{-0,3306}}{L}$$, the value of G is constant at 2880 mL/menit, and so

$$t = 2551,92/L \quad \ldots\ldots (4).$$

Furthermore, equation (4) is used to calculate the residence time at various total flow rate of material entering the research conducted. Relations residence time, t minutes with L, mL/min as in table II.

Table II. Relations residence time, t, with a total solution velocity, L

Kecepatan larutan total (1:1), mL/menit	Waktu tinggal, t menit
28,4	89,86 ≈ 90
31,2	81,79 ≈ 82
35,4	72,09 ≈ 62
42	60,76 ≈ 61
48,6	52,50 ≈ 53

More results are shown in Table III guidelines pectin results of 600 ml of filtrate, based on the calculation of mass balance cocoa peel solids, while the concentration (%) methoxyl calculated based on the equation (1). More results shown in the Figure 4.

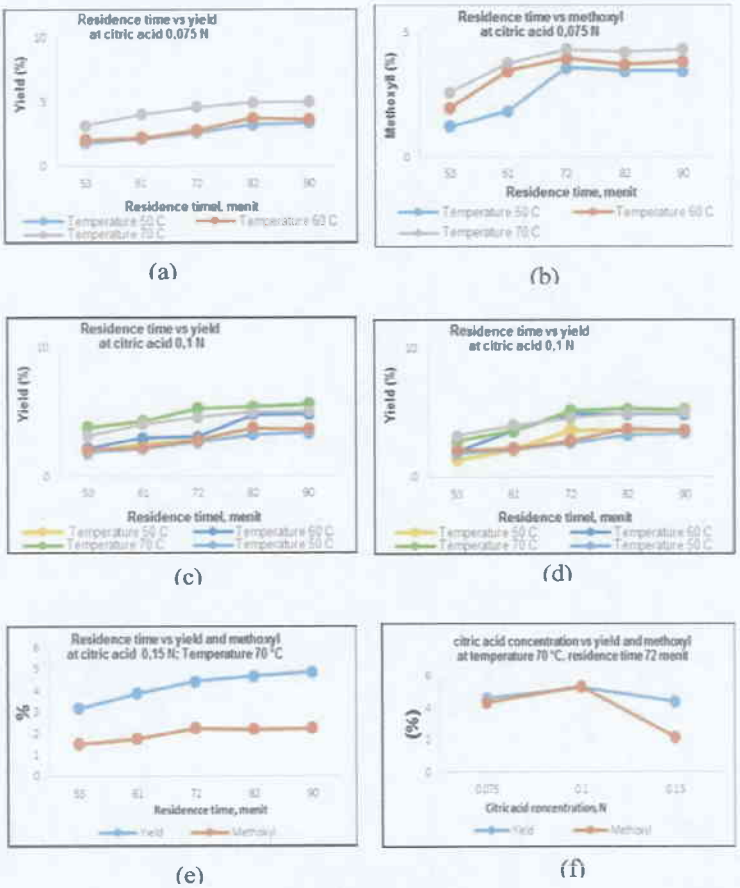


Figure 4. Result research

From Figure 4 (f) it is clear that the concentration of citric acid heavily influence the yield and content of methoxyl. If seen the best results from this study occurred at 70 °C and citric acid concentration of 0.1 N Guided by the quality of the pectin is indicated by the methoxyl content, the best results occur when residence time material in the reactor for 82 minutes with the highest level of methoxyl, namely 5,332%.

Conclussion

The conclusion that can be write from the results that have been achieved are :

1. Liquid residence time calculated with equation (V-3): $t = \frac{12931{,}22\,G^{-0{,}3306}}{L}$ menit

2. Based on pectin quality, the best result can be obtained at temperature 70 °C, citric acid concentration 0,1 N with material residence time in the reactor is 82 minutes, with metoksil concentration is 5,332%.

Refference :

Ankrah, E.K., 1974, Chemical studies of some plant wastes from Ghana, *J.Sci. Fd. Agric.* 25: 1229-32.

Bhornsmithikun, V., Chetpattananondh, P., Yamsaengsung, R., and Prasertsit, K. 2010. Continuous Extraction Of Prebiotics From Jackfruit Seeds. Songklanakarin J. Sci. Technol. 32 (6), 635-642.

CPCelco, 2010, *"Genu Pectin Book"*, www.cpcelko.com.

Daryono, E.,D., 2012, Ekstraksi Pektin dari Labu Siam, *Jurnal Teknik Kimia* Vol. 7, No. 1: 22-25

Gentilini, R., Bozzini, S., Munarin, F., Petrini, P., Visai, L., Tanzi, M., 2014, Pectins from *Aloe Vera*: Extraction and Production Of Gels For Regenerative Medicine. *J. Appl. Polym. Sci.* 131.Issue 2.

Hanum, F., Kaban, I. M. D., Tarigan, M. A, 2012, Ekstraksi Pektin dari Kulit Buah Pisang Raja (*Musa sapientum). Jurnal Teknik Kimia USU* Vol. 1, No. 2: 21-26

Harriott, P., 2003, *"Chemical Reactor Design"*, Marcel Dekker, Inc, New York.

Ismail, N. S. M., Ramli, N., Hani, N. M., dan Meon, Z., 2012, Extraction and Characterization of Pectin from Dragon Fruit (*Hylocereus polyrhizus)* using Various Extraction Conditions. *Sains Malaysiana* Vol. 41 No. 1: 41-45

Kim, K. H., Melvin P. Tucker, M. P., Fred A. Keller, F. A., Aden, A., and Nguyen, Q. A., 2001, Continuous Countercurrent Extraction Of Hemicellulose From Pretreated Wood Residues, *Applied Biochemistry and Biotechnology* Vol. 91–93, pp. 253-267

Malviya, R., Srivastava, P., Bansal, M., and Sharma, P. K., 2010, Mango Peel Pectin as a Superdisintegrating Agent. *Journal of Scientific & Industrial Research* Vol. 69, September 2012: 668-890

M. C. Golberg, L., DeLong, and Kahn, L., 1971, Continuous extraction of organic materials from water, *Journal of Environmental Science and Technology*, vol. 5, issue 2, pp. 161-162

Pardede, A., Ratnawati, D., dan Martono HP, A., 2013, Ekstraksi dan Karakterisasi Pektin dari Kulit Kemiri (*Alleurities mollucana Willd). Media SainS* Vol. 5 No. 1: 66-71

Perry, R.H., and Chilton, C.H,1973, *"Chemical Engineers' Handbook"*. 5th ed. pp.2-128. McGraw-Hill Kogakusha, Ltd., Tokyo.

Rase, H.F. 1977. *Chemical Reactor Design for Process Plants, Volume One: Principles and Techniques.* John Wiley & Sons, New York.

Sari, E., Praputri, E., Rachmat, A., dan Okdiansyah, A., 2012, Peningkatan Kualitas Pektin dari Kulit Kakao melalui Metode Ekstraksi dengan Penambahan $NaHSO_3$. *Prosiding SNTK TOPI 2012*. ISSN 1907-0500. p. 47-52, Pakanbaru

Shin, S. B., Han, S. P., Lee, W. J., Im, Y. H., Chae, J. H., Lee, D. I., and Lee, W. H, 2007, Optimize Terephthaldehyde Reactor Operations. Process Systems Enterprise Ltd., London, United Kingdom. *Hydrocarbon Processing*

Soemargono dan Billah, M. 2007, Pembuatan Kalsium Karbonat dari Bittern dan Gas Karbon Dioksida secara Kontinyu. *Jurnal REAKTOR Teknik Kimia FT-UNDIP*, Vol.11,No.1 Juni 2007:14-21

Soemargono, Mulyadi, E., Priyanto, B., Susilowati, Sasongko, P. E., Edahwati, L., dan Yulistiani, R., 2013, Pengelolaan Limbah Kakao Berbasis Teknologi Ramah Lingkungan di Kabupaten Blitar. *Prosiding Seminar Nasional Pengembangan Luaran Penelitian Mendukung Dunia Industri*. LPPM-UPN "Veteran" Jawa Timur. ISSN 978-602-9372-63-2. P. 8-14. Surabaya.

Stephen, A. M., 1995, *"Food Polysaccharides and Their Applications"*, pp.287-323. Marcel Dekker, Inc. New York.

Susilowati, Munandar, S., Edahwati, L., dan Sihana. 2010. Ekstraksi Pektin dari Kulit Buah Coklat dengan Pelarut Asam Sitrat. *Jurnal Ilmiah EKSERSI* Vol. XI, No. 1, Juni 2013: 25-28

Stangle, G.C., and Mahalingam, R., 1990, Mass Transfer with Chemical Reaction in a Three-Phase Foam-Slurry Reactor, *A. I. Ch. E. Journal*,36, 117-125.

Stephen, A. M. 1995. *Food Polysaccharides and Their Applications.* Marcel Dekker, Inc. New York.

Wood, G.A.R. & R.A. Lass. 1985. Cacao. Longman Group Limited, New York, 620p.

Zehner, P and Kraum, M. 2000. Bubble Columns. http://www.researchgate.net/ publication/228033687